REMOVAL OF SUSPENDED SOLIDS FROM LIME-SULFIDE UNHAIRING EFFLUENTS*

E. H. BITCOVER, J. E. COOPER, W. F. HAPPICH†, AND E. M. FILACHIONE

Eastern Regional Research Center‡
Philadelphia, Pennsylvania 19118

ABSTRACT

Seven new polyelectrolytes were evaluated as flocculants and coagulants for removing suspended solids from highly alkaline, lime-sulfide, hair-pulping effluents from a hide processor. Six of these are chemical derivatives of starch with acrylic acid or acrylamide, and the seventh is a copolymer product of acrylic acid and acrylamide. Four of these polyelectrolytes were effective at levels of 5 to 25 p.p.m., without pH adjustment of the effluent, and reduced the suspended solids about 95 percent. No auxiliary agents were required to assist in the coagulation of the suspended solids. The moisture contents of the flocculated settled solids ranged from 50 to 75 percent.

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INTRODUCTION

As of July 1, 1977, the tanning industry is required to conform to the first set of EPA limitations defining the quality of effluents discharged to the environment (1). The compositions of tannery effluents are complex and variable, and the detrimental effects of these effluents discharging into the environment are well known. Lately there has been much research involving physical, chemical, and biological processes for treating these effluents to reduce toxic and undesirable components to acceptable levels. Sedimentation by gravity removes readily settleable solids. Chemical treatment removes most of the remaining suspended and precipitable solids by flocculation or coagulation. Biochemical treatments reduce soluble biological oxygen demand (BOD) and sulfide of unhairing effluents (2).

Following sedimentation, the remaining insoluble solids of unhairing effluents are essentially colloidal suspensions of pulped hair, lime particles, fat, and other hide residuals. Colloidal suspensions have electrical charges because of preferential adsorption of cations or anions from solution. A colloidal suspension will flocculate when an electrolyte providing readily adsorbable ions of the opposite electrical charge is added. Chemical coagulants bring the particles of the effluent together

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†Retired.

‡Agricultural Research Service, U. S. Department of Agriculture.

into intimate contact to form settleable or filterable solids by neutralizing their electrical charges and forming heavy particles or precipitates. Friberg and Roberts (3) showed an extremely efficient way of flocculating colloidal particles by the addition of polymers having charged groups. The mechanism is considered to be a molecular bridging between the particles with loops of the polymer chain. However, complete enclosing of the particles by polymer produces protection of the particles *against* flocculation, so that the optimum concentration of polymer effecting flocculation should not be exceeded.

Papazov and Karchev (4) described various coagulation methods used to purify tannery wastes in a model Bulgarian tannery. They studied the use of $FeSO_4$, $FeCl_3$, and $Al_2(SO_4)_3$, and recommended $FeSO_4$ as the most convenient chemical coagulant. Simoncini *et al.* (5) reported considerable reductions in total solids, BOD, and chemical oxygen demand (COD) in screened tannery unhairing effluent by the use of $FeSO_4$, $ZnSO_4$, or $Al_2(SO_4)_3$, and reported that $FeSO_4$ produced the most rapid sedimentation and the most readily dried sludge. Ludvik *et al.* (6) treated effluents in a Czechoslovakian tannery by mechanical means (sedimentation, screening, filtering), followed by biological treatment. These treatments produced sludges suitable for fertilizer purposes and waste waters suitable for discharge to the environment. Cooper *et al.* (7) reported that the addition of organic polyelectrolytes such as Rohm and Haas Company products PFA-10** (anionic), followed by PFC-3 (cationic), and lastly sodium hexametaphosphate (an inorganic polyelectrolyte), added in that order, reduced the suspended solids by 98 percent in a conventional paddle vat, hair-burn effluent.

This paper reports the effectiveness of seven new organic polyelectrolytes as flocculating agents for the removal of suspended solids from a highly alkaline, hair-pulping, lime-sulfide effluent originatitng in a hide processor.

EXPERIMENTAL

The unhairing effluent used in these studies was obtained from a tanner who unhairs salt cured hides in a hide processor by the high-sulfide, hair-pulping process. The full strength effluent was obtained directly from the unhairing operation. It also contained the salt from the hide soaking operation, but did not include any wash water.

Flocculating Agents

The newly-developed polyelectrolytes evaluated as flocculants and coagulants (Table I) included six graft copolymers of cereal starches and flours with acrylic acid or acrylamide, developed jointly by the Northern Regional Research Center, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois, and General Mills Chemicals, Inc., Minneapolis, Minnesota, and an acrylic acid-acrylamide copolymer, X-400, available from Estech, Inc., Chicago, Illinois.

**Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

TABLE I

EXPERIMENTAL FLOCCULATING AGENTS

Polyelectrolyte	Type	Composition
SGP-20	Cationic	Starch-Acrylamide
SGP-21	Cationic	Starch-Acrylamide
SGP-30	Anionic	Starch-Acrylic Acid
SGP-100	Nonionic	Starch-Acrylamide
SGP-502	Anionic	Starch-Acrylonitrile
SGP-523	Anionic	Starch-Acrylonitrile
X-400	Anionic	Acrylic Acid-Acrylamide

One percent solutions of each polyelectrolyte were prepared by dispersing one gram of the solids into the vortex of 100 ml. of water stirred magnetically and heated to about 65°–75°C. Aliquots of these stock solutions were used in the tests.

These polyelectrolytes were used as additives to screened unhairing effluent without any prior pH adjustments of the effluent. Each polyelectrolyte was first assessed in a preliminary series of tests. They were used alone and in combination with Rohm and Haas Company products PFA-10, PFC-3, and sodium hexametaphosphate solutions.

Flocculation Procedure

The general procedure followed in these studies was similar to that reported by Cooper *et al.* (7). The effluent as received was put through a 50 x 50 mesh polypropylene screen to remove the large solid particles. One liter samples of screened effluent were transferred to six 1500 ml. beakers and stirred at 100 r.p.m. with a Phipps & Bird apparatus while the flocculating reagents were added. Aliquots of one percent polyelectrolyte solution were pipetted into the beakers to provide a range of concentrations of polyelectrolyte from 0 to 100 mg./l. in the effluent at intervals of 20 mg./l. In those instances where the first polyelectrolyte used was cationic, the anionic PFA-10 (3.0 mg./l.) was added second, and lastly sodium hexametaphosphate (30 mg./l.). If the first polyelectrolyte was anionic, the cationic PFC-3 (0.3 mg./l.) was added next, and lastly sodium hexametaphosphate. The SGP-100, a nonionic type, was followed only by sodium hexametaphosphate. The stirring rate was maintained for five minutes at 100 r.p.m., after which it was decreased to 25 r.p.m. for an additional 20 minutes to promote floc formation. Where more than one reagent was added, the sample was stirred for five minutes at 100 r.p.m. after each addition, prior to stirring at 25 r.p.m. for an additional 20 minutes. Then the floc was allowed to settle for 30 minutes, after which 10 ml. of the supernatant liquor was pipetted from 2.5 cm. below the surface for determination of suspended solids.

The polyelectrolyte concentration effecting the greatest reduction in suspended solids was used as the reference point for additional test series to determine the most effective polyelectrolyte concentration in the effluent. Concentrations of polyelectrolyte at smaller intervals were selected. Samples were taken from the supernatant liquors 2.5 cm. below the surface after 30 minutes settling for determinations of suspended solids, total alkalinity, total nitrogen, organic nitrogen, sodium sulfide, and chemical oxygen demand.

Calcium Oxide Content of Suspended Solids

Since lime is used in excess quantities for unhairing hides, the lime content of the suspended solids of the unhairing solutions is of great interest. Two polyelectrolytes, SGP-100 and X-400, were selected to find the effects of these flocculating agents on the lime content of the suspended solids. The optimum concentration of these polyelectrolytes (6 mg./l.) was used. After the usual flocculation procedure, 10 ml. of the supernatant liquors were pipetted from 2.5 cm. below the surface for determinations of calcium oxide in solution and in the suspended solids. Each sample was introduced into a 100 ml. round-bottom boiling flask, 25 ml. of 2 N hydrochloric acid was added, and then the mixture was refluxed about four hours. After being cooled, the samples were filtered through No. 42 Whatman paper into 250 ml. volumetric flasks. The filters were washed several times with hot deionized water and the washings were collected in the volumetric flasks, which were then filled to volume with deionized water. These solutions were analyzed for calcium oxide contents by an atomic absorption method. The residues from ignition of the suspended solids at 600°C. were also analyzed for calcium oxide by transferring them into 100 ml. round-bottom boiling flasks, adding 30 ml. of 2 N hydrochloric acid, and refluxing them for four hours. The solutions were filtered and washed, as described above, and were then analyzed for calcium oxide content by the atomic absorption method.

Moisture Content of Settled Solids

The moisture contents of the flocculated, settled solids at the bottoms of the beakers, after 30 minutes settling, were determined after decanting the supernatant liquors and transferring the residues into weighed porcelain evaporation dishes. The residues were heated on a steam bath, with occasional stirring, and finally dried overnight at 105°C. in a drying oven. The loss in weight was calculated as loss of moisture.

Analytical Methods

The official methods of analysis of the American Public Health Association, American Water Works Association, and the Water Pollution Control Federation were used for the determinations of pH, COD, total solids, total volatile solids, suspended solids, volatile suspended solids, and alkalinity, and settleable solids (8). Total and organic nitrogen were determined by the semi-micro Kjeldahl method (9). Sodium sulfide was determined by the Official Method of

Analysis of the Society of Leather Trades' Chemists (10). Calcium oxide was determined with a Perkin-Elmer Model 306 Atomic Absorption Spectrophotometer equipped with a triple-slot burner (11, 12).

RESULTS AND DISCUSSION

Composition of Lime-Sulfide Effluent

A typical composition of the screened hide processor lime-sulfide unhairing effluent is shown in Table II. The composition of a typical screened paddle vat effluent reported previously by Happich *et al.* (13) is included for comparison.

TABLE II

COMPOSITION OF SCREENED LIME SULFIDE UNHAIRING EFFLUENTS

	Paddle Vat* (Fresh Hides)	Hide Processor (Cured Hides)
Chemical Oxygen Demand, mg./l.	36,640	62,390
Total Solids, mg./l.	56,900	207,800
Total Volatile Solids, mg./l.	36,160	35,600
Suspended Solids, mg./l.	25,450	46,550
Volatile Suspended Solids, mg./l.	16,790	22,100
Total Alkalinity ($CaCO_3$), mg./l.	15,195	38,710
pH	12.8	12.7
Na_2S, percent	0.55	1.14
Total Kjeldahl N, percent	0.41	0.51
Organic N, percent	0.38	0.48
Settleable Solids, ml./l.**	300	75

*Reported previously by Happich *et al.* (13).
**After 30 min. at 25°C.

There are considerable differences between these screened effluents. The high total solids content of the hide processor effluent is due to the fact that this tanner soaks cured hides and then adds unhairing chemicals to soak liquor without dumping the soak water.

Effect of Polyelectrolyte Concentration on Removal of Suspended Solids

Table III summarizes the results of the various tests for reducing suspended solids in hide processor, lime-sulfide unhairing effluent. The experiments were performed in duplicate and the average deviation of the replicates was of the order of five percent or less. The suspended solids content of the screened effluent was 46,550 mg./l., and gravity settling for 30 minutes reduced it to 25,660

TABLE III

MOST EFFECTIVE CONCENTRATION OF POLYELECTROLYTE FOR REMOVAL OF SUSPENDED SOLIDS FROM HIDE PROCESSOR UNHAIRING EFFLUENT

Polyelectrolyte		Suspended Solids*	
Type	Concentration (mg./l.)	(mg./l.)	Percent Reduction
Control**		25,660	45.0
SGP-20	20	3,000	93.6
SGP-21	20	28,100	39.6
SGP-30	20	2,390	94.9
SGP-100	6	2,120	95.4
SGP-502	20	24,580	47.2
SGP-523	20	31,640	32.0
X-400	6	1,260	97.3

*Suspended solids of screened effluent after settling 30 min. Original value, 46,550 mg./l.

**No polyelectrolyte added.

mg./l. This represents a 45 percent reduction in suspended solids by gravity sedimentation alone. Four of the polyelectrolytes effectively reduced suspended solids by more than 90 percent, based on reductions from 46,550 mg./l. The other polyelectrolytes did not exhibit similar flocculating abilities under the conditions of the tests. SGP-20 and SGP-30 were most effective at a concentration of 20 mg./l. of effluent; SGP-100 and X-400 were most effective at 6 mg./l.

Effect of Auxiliary Polyelectrolytes on Removal of Suspended Solids

Cooper *et al.* (7) reported that 3 mg./l. of PFA-10, 0.3 mg./l. of PFC-3, and 30 mg./l. of $(NaPO_3)_6$, added in that order, reduced the suspended solids of paddle vat unhairing effluent about 98 percent. Table IV shows the effects of the addition of these materials as auxiliary agents to the new experimental polyelectrolytes used for hide processor unhairing effluent. With the four recommended polyelectrolytes the addition of these auxiliary agents produced little or no additional reduction of suspended solids, and in some cases decreased the percentage reduction of suspended solids.

Effect of Polyelectrolytes on Calcium Oxide Content of Suspended Solids

Table V shows the calcium oxide contents of suspended solids of hide processor unhairing effluent treated with 6 mg./l. of SGP-100 or X-400. There is considerable reduction in the calcium oxide content of the suspended solids, from approximately one percent CaO in the control to approximately 0.1 percent CaO in the polyelectrolyte-treated effluents. The ignited residues of the suspended

TABLE IV

EFFECT OF AUXILIARY POLYELECTROLYTES ON REDUCTION OF SUSPENDED SOLIDS FROM SCREENED HIDE PROCESSOR UNHAIRING EFFLUENT

Polyelectrolyte		Percent Reduction of Suspended Solids					
			Added Auxiliary Agent				
Type	Concentration (mg./l.)	Polyelectrolyte Alone	PFA-10*	PFC-3†	$(NaPO_3)_6$‡	PFA-10*+ $(NaPO_3)_6$‡	PFC-3†+ $(NaPO_3)_6$‡
SGP-20	20	93.6	82.5	N.A.	N.A.	53.6	N.A.
SGP-30	20	94.9	N.A.	29.8	N.A.	N.A.	29.3
SGP-100	6	95.4	N.A.	N.A.	67.8	N.A.	N.A.
X-400	6	97.3	N.A.	89.5	N.A.	N.A.	88.8
PFC-3	0.3	9.3	—	—	—	86.3	—
PFA-10	3	58.4	—	—	—	—	86.3
$(Na\ PO_3)_6$	30	83.0	—	—	—	—	—

N.A. = Not Applicable.
*3 mg./l.
†0.3 mg./l.
‡30 mg./l.

TABLE V

EFFECT OF ORGANIC POLYELECTROLYTES ON CALCIUM OXIDE CONTENT OF SUSPENDED SOLIDS IN HIDE PROCESSOR LIME-SULFIDE UNHAIRING EFFLUENT

Polyelectrolyte Type	Concentration (mg./l.)	CaO Content of Suspended Solids (%)	Ash Content of Suspended Solids (%)	CaO Content of Ash (%)	CaO Content of Settled Solids (%)
Control		1.12	40.7	79.07	20.93
SGP-100	6	0.14	48.0	27.75	72.25
X-400	6	0.09	55.5	35.09	64.91

solids showed reductions from approximately 80 percent CaO in the control to approximately 30 percent CaO in the test examples. These results indicate that the major inorganic component of the suspended solids is lime and that most of the lime settles out with the flocculated solids.

Effect of Polyelectrolyte Concentration on Composition of Hide Processor Lime-Sulfide Effluent

The effects of SGP-100 and X-400 are shown graphically in Figures 1 and 2. There were very little changes in the nitrogen, COD, and sodium sulfide values.

The effluents contain high levels of soluble nitrogen-containing compounds and high sulfide ion levels which contribute to high COD values and which are not removed by treatment with organic polyelectrolytes. Further chemical or biological treatments are necessary to remove these constituents before the effluent can be safely discharged to municipal waste treatment plants or to streams.

Figure 1 illustrates the response to increasing levels of SGP-100. Use of 3 to 6 mg./l. clearly produced the most effective results, reducing total suspended solids by 95 percent, volatile suspended solids by 97 percent, and total alkalinity

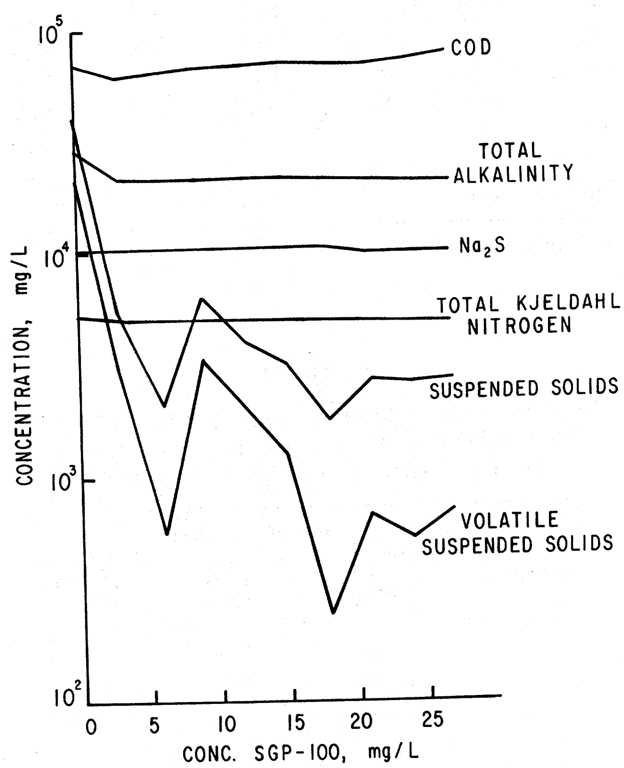

FIGURE 1.—Effect of SGP-100 Concentration Upon Composition of Hide Processor Unhairing Effluent.

by 30 percent. As can be seen by the curves, higher levels of polyelectrolyte are less effective. First and second optimum concentrations, a phenomenon common in use of flocculating agents (7), are shown.

Similar results are seen for X-400 (Figure 2), with the optimum concentration in the 3 to 9 mg./l. range. Total suspended solids were reduced 97 percent, volatile suspended solids 99 percent, and total alkalinity 45 percent.

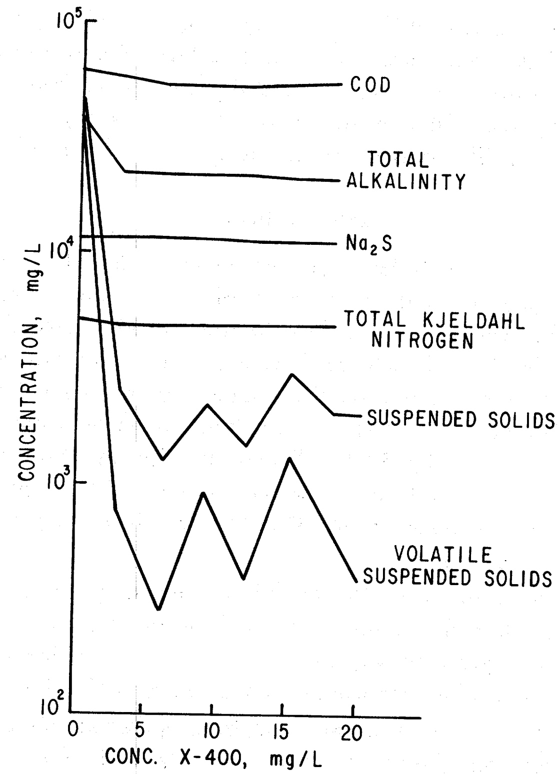

FIGURE 2.—Effect of X-400 Concentration Upon Composition of Hide Processor Unhairing Effluent.

Moisture Content of Flocculated Solids

Table VI shows the moisture contents of the flocculated settled solids obtained at 95 percent suspended solids removal for the four most effective flocculants compared with the control at 45 percent removal. The moisture contents varied from about 48 to 75 percent, whereas the moisture content of the solids from

TABLE VI

MOISTURE CONTENTS OF FLOCCULATED SETTLED SOLIDS

Polyelectrolyte Type	Concentration (mg./l.)	Moisture (%)
Control	—	70.0
SGP-20	20	61.6
SGP-30	20	73.0
SGP-100	6	48.2
X-400	6	59.3

the control was 70 percent. SGP-100 used at 6 mg./l. is clearly superior in producing a high solids content precipitate. Since solids removed must be dried for disposal, the moisture content of the settled solids is an important criterion. Ludvik *et al.* (6) reported that sludge dewatered to a dry matter content of 25 percent can be readily transported and used directly for fertilizing.

CONCLUSIONS

Of seven new organic polyelectrolytes evaluated as flocculants and coagulants for removing suspended solids from screened, hair-pulping, lime-sulfide, hide processor unhairing effluent, two, SGP-100 and X-400, caused flocculation and were effective at levels of 3 to 6 mg./l. concentration; two others, SGP-20 and SGP-30, were as effective, but required higher concentration levels. They reduced suspended solids by 93–97 percent, volatile suspended solids by 95–99 percent, and total alkalinity by 30 to 45 percent. The moisture contents of the settled solids were reduced from 70 percent to about 50 percent, and the lime (CaO) content was increased from 20 percent to about 70 percent by the use of these flocculating agents.

It is not necessary to adjust the pH of the effluent prior to addition of the recommended polyelectrolytes, nor is the pH of the effluent changed by their addition. This is of great advantage since it prevents the liberation of noxious hydrogen sulfide, a process that would occur at lower pH values.

This effluent from a hide processor unhairing operation contained high levels of soluble nitrogen-containing organic compounds (solubilized keratin, amino acids, and peptides), high sulfide ion levels, and fats, so that, even if total removal of suspended solids were effected, further biological or chemical treatments would be required before discharge. The principal value of these polyelectrolytes is their removal of substantial amounts of the pollution load from a hide processor unhairing effluent in a simple operation prior to secondary treatment or reuse of the unhairing solution.

ACKNOWLEDGMENTS

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DISCUSSION

MR. SATYENDRA M. DE (Chestnut Operating Company): Thank you, Dr. Bitcover, for an excellent paper. Dr. Bitcover and his coworkers have presented a very nice paper dealing with the removal of suspended solids from beamhouse waste waters which should interest every tanner. We know that suspended solids are one of the pollution loads that create problems in effluent treatments. The EPA wants BOD_5 and suspended solids removal, and, especially when suspended solids are removed, BOD_5 will also be removed.

However, in this paper we find that COD and total nitrogen are not affected, while suspended solids are removed. I would appreciate Dr. Bitcover's comments on this point.

DR. BITCOVER: The COD was reduced about twenty percent. I think that most of the nitrogen-containing compounds are in solution.

MR. DE: Can the by-product suspended solids you recover be used for any purpose?

DR. BITCOVER: We are setting up a chicken feeding test to evaluate this material as a feed source.

MR. ROBIN RAPPORT (Seal Tanning Company): What is the BOD_5 value on the treated material?

DR. BITCOVER: We did not determine BOD_5 values. We know that the BOD_5 is approximately 2/3 or 3/4 of the COD.

Mr. Rapport: Do you have any analytical data on the recovered suspended solids?

Dr. Bitcover: Not at this time.

Mr. Rapport: Why did you use sodium hexametaphosphate?

Dr. Bitcover: I was continuing work done earlier by Mr. Cooper on paddle vat effluents. The hexametaphosphate is not necessary with these new polyelectrolytes on the hide processor effluents.

Mr. Rapport: Why do the effluents from the paddle vat and hide processors differ so much?

Dr. Bitcover: The soak liquors with the removed salt are not dumped in the hide processor. So the waste waters contain the salt, the increased unhairing chemicals, and the greater level of hair pulp.

Dr. Robert M. Lollar (Tanners' Council of America): What feed nutrients do you expect in your precipitates if the treatments are not removing Kjeldahl nitrogen?

Dr. Bitcover: There is some hair and a lot of lime. Calcium is very important in egg shell formation.

Dr. Ross G. Donovan (Canada Packers Ltd.): Thank you, Dr. Bitcover.